

Supplementary Information

**Tristate ferroelectric memory effect attained by tailoring the
ferroelectric behavior in $\text{Bi}_{1/2}(\text{Na}_{0.8}\text{K}_{0.2})_{1/2}\text{TiO}_3$ with Eu doping**

Yang Hu,^a Huazhang Zhang,^{a,b} Jing Zhou,^{a,c} Jie Shen,^a Binbin Chen,^a Ang Li,^a Wen
Chen^{*a}

^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China

^b Department of Physics, School of Sciences, Wuhan University of Technology, Wuhan 430070, P. R. China

^c Sanya Science and Education Innovation Park of Wuhan University of Technology, Sanya 572025, P. R. China

* Corresponding author: Prof. Wen CHEN

* E-mail address: chenw@whut.edu.cn

Table S1. The final compositions of the synthesized $(\text{Bi}_{1-x}\text{Eu}_x)_{1/2}(\text{Na}_{0.8}\text{K}_{0.2})_{1/2}\text{TiO}_3$ ceramics with different Eu doping contents, characterized by ICP (for Bi, Eu and Ti) and AAS (for Na and K), where the composition of Ti is normalized to 1. The values within the brackets are the theoretical compositions.

| <i>x</i> | Bi | Eu | Na | K | Ti |
|-----------------|----------------------|----------------------|--------------------|--------------------|--------------|
| 0.0% | 0.500 (0.500) | 0 (0) | 0.391 (0.4) | 0.097 (0.1) | 1 (1) |
| 1.0% | 0.496 (0.495) | 0.005 (0.005) | 0.392 (0.4) | 0.097 (0.1) | 1 (1) |
| 2.0% | 0.492 (0.490) | 0.010 (0.010) | 0.390 (0.4) | 0.096 (0.1) | 1 (1) |
| 3.0% | 0.485 (0.485) | 0.015 (0.015) | 0.392 (0.4) | 0.097 (0.1) | 1 (1) |
| 4.0% | 0.481 (0.480) | 0.021 (0.020) | 0.391 (0.4) | 0.096 (0.1) | 1 (1) |
| 5.0% | 0.474 (0.475) | 0.025 (0.025) | 0.394 (0.4) | 0.096 (0.1) | 1 (1) |

Table S2. Bulk density and relative density of the as-prepared BNKT: x Eu samples.

| Eu content, x (%) | Density (g/cm ³) | Relative density (%) |
|---------------------|------------------------------|----------------------|
| 0.0 | 5.872 | 97.55 |
| 1.0 | 5.846 | 97.11 |
| 2.0 | 5.872 | 97.53 |
| 3.0 | 5.872 | 97.54 |
| 4.0 | 5.891 | 97.86 |
| 5.0 | 5.878 | 97.65 |

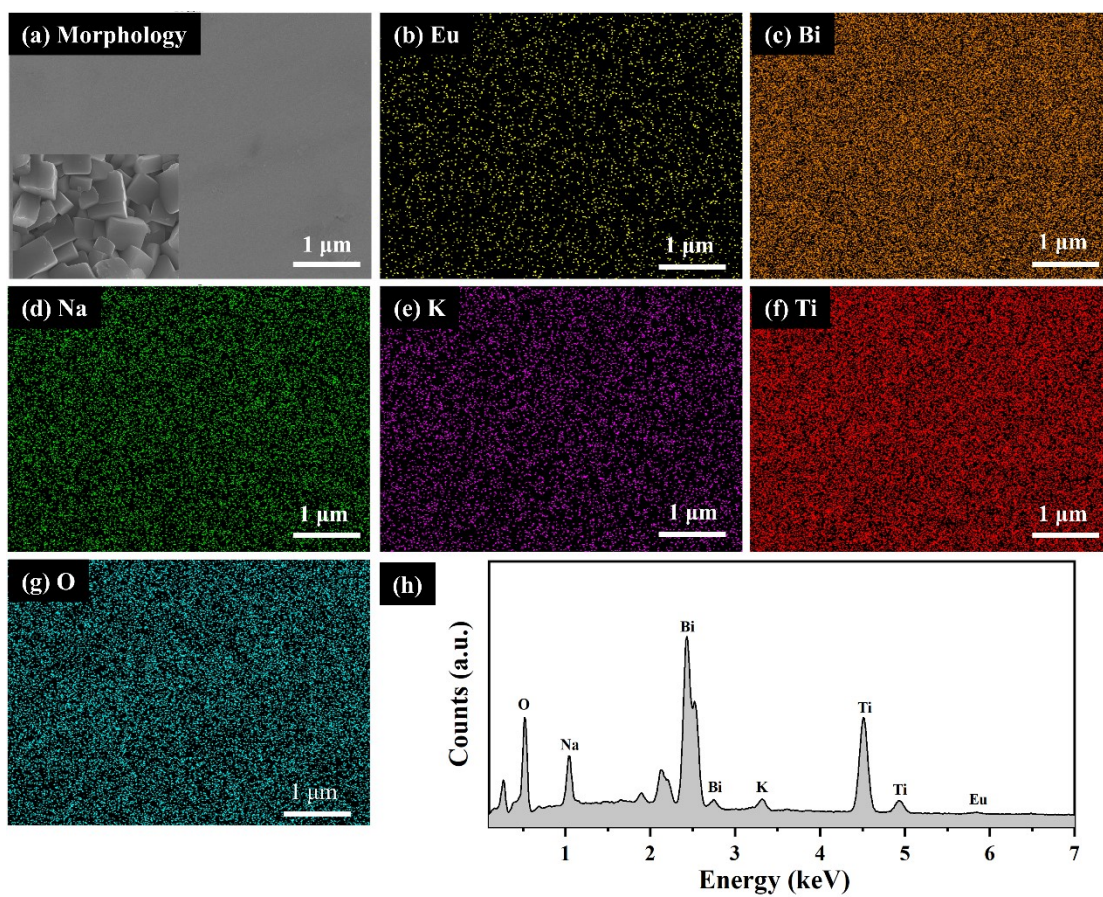


Fig. S1 (a)The morphology of polished surface; the elements mapping of (b) Eu, (c) Bi, (d) Na, (e) K, (f) Ti, (g) O, and (h) the EDS patterns of BNKT:3.0%Eu.

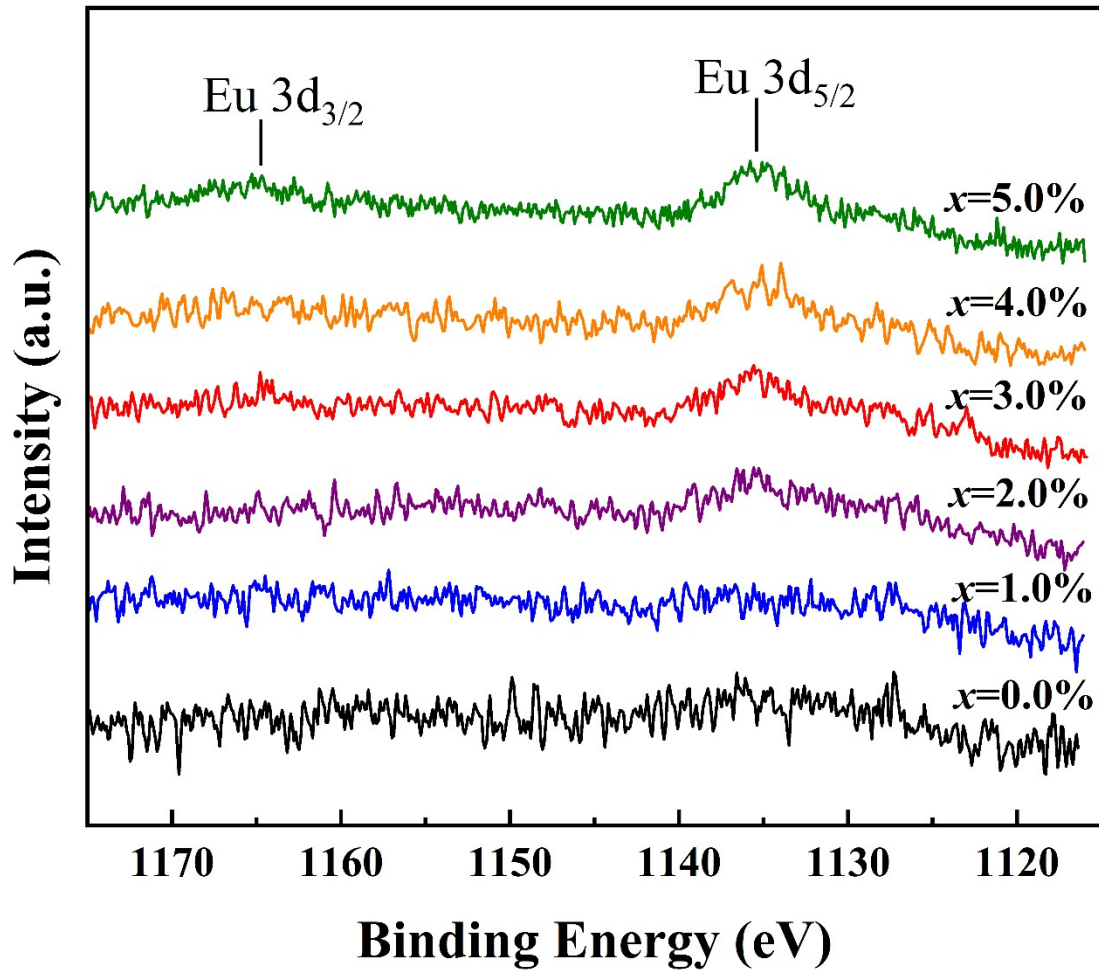


Fig. S2 The Eu 3d spectra of the BNKT:*x*Eu ceramics by XPS characterization. For the samples with $x = 0.0\%$ and $x = 1.0\%$ samples, the signal of the Eu element cannot be detected, due to the low Eu content. As for other samples, a pair of relatively low intensity of peaks around 1135 and 1165 eV are detected, which are corresponding to Eu³⁺ oxidation state.

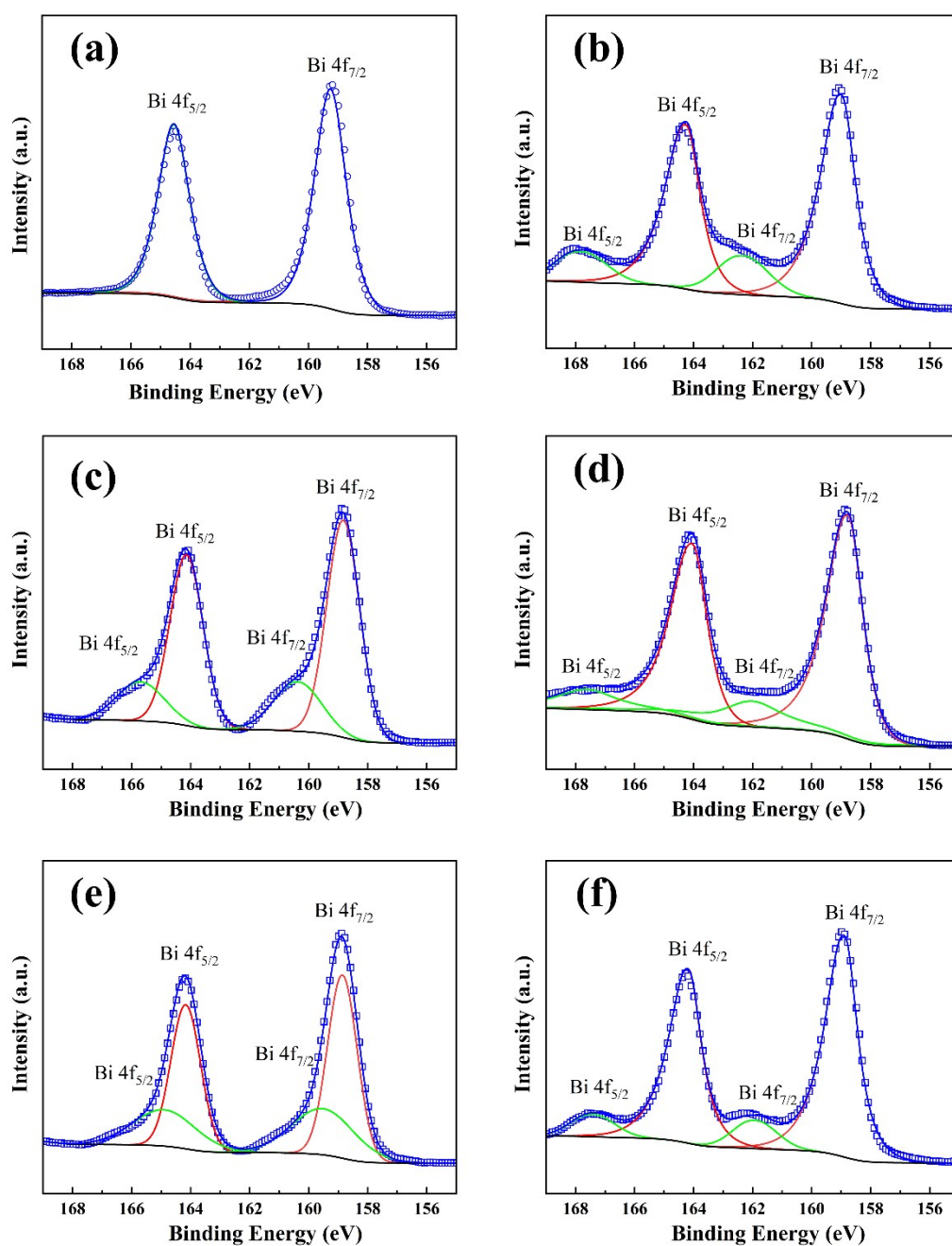


Fig. S3 The Bi 4f spectra of the BNKT: x Eu ceramics by XPS characterization. (a) $x=0.0\%$; (b) $x=1.0\%$; (c) $x=2.0\%$; (d) $x=3.0\%$; (e) $x=4.0\%$ and (f) $x=5.0\%$. Compared with (a) the pure BNKT, there is a pair of additional peaks of Bi $4f_{7/2}$ and Bi $4f_{5/2}$ in (b-f) the Eu doped sample. This phenomenon could be due to that the Eu substitutes at the A-site and change the chemical environment of Bi.

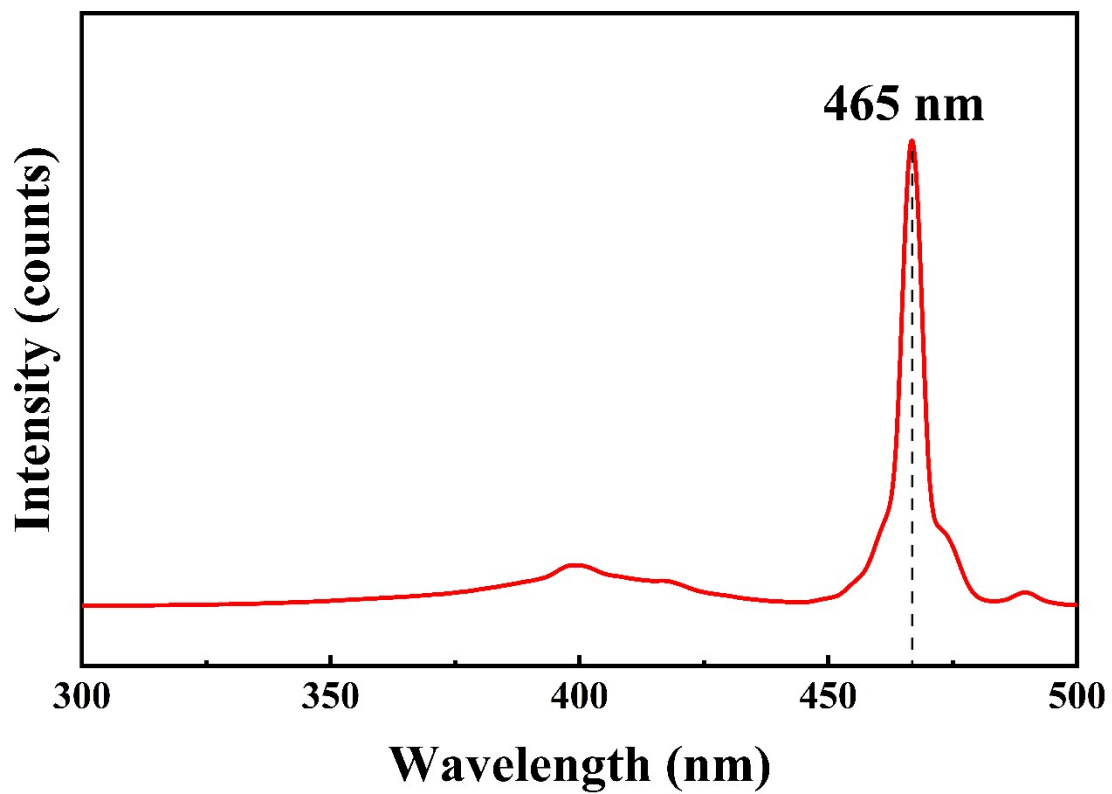


Fig. S4 The excitation spectra of Eu³⁺ when emission wavelength is 615 nm. The measurement is conducted on BNKT:3.0%Eu as a representative.

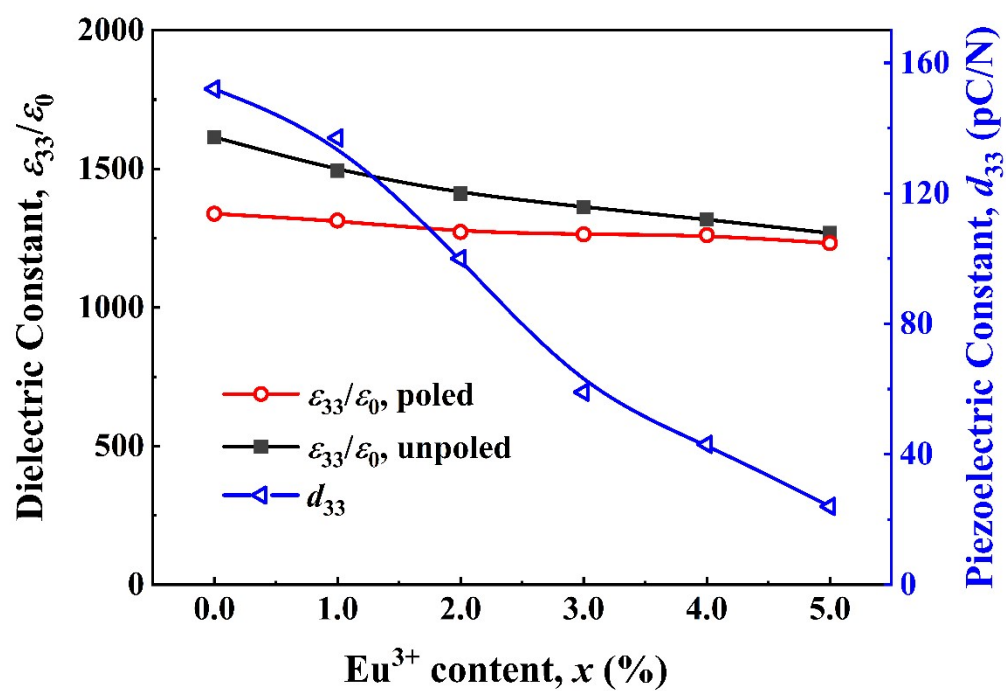


Fig. S5 Dielectric and piezoelectric constants of BNKT: x Eu.

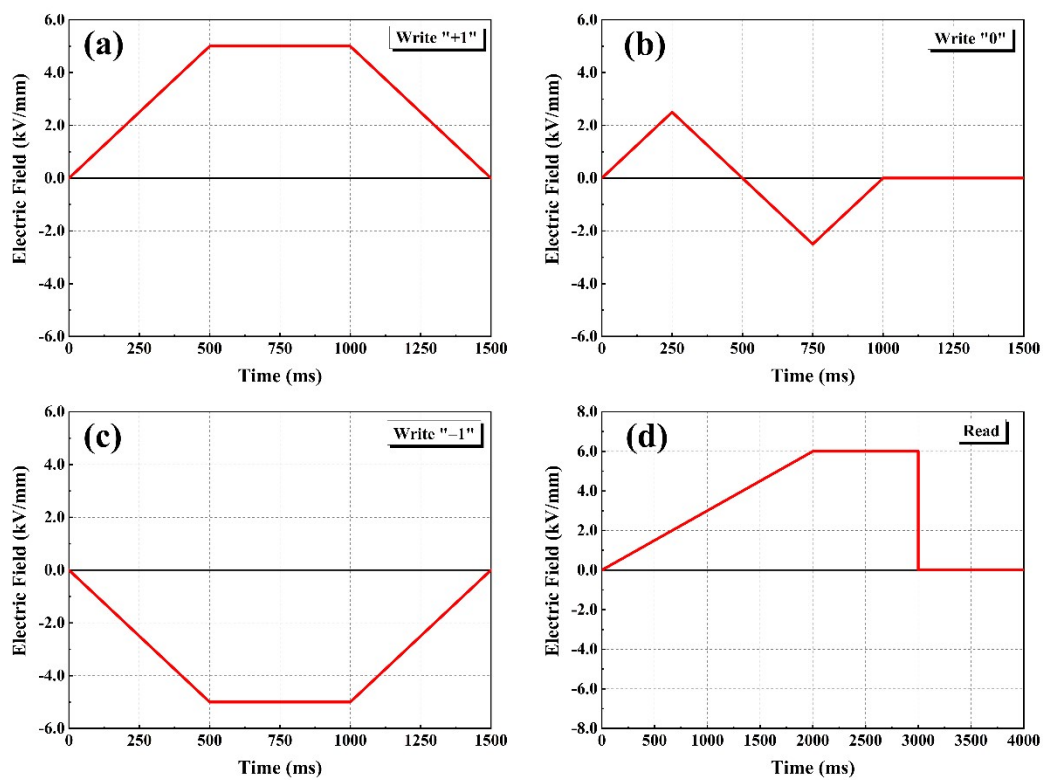


Fig. S6 Write/read electric field waveforms. (a) Write "+1" state; (b) write "0" state; (c) write "-1" state; and (d) read.

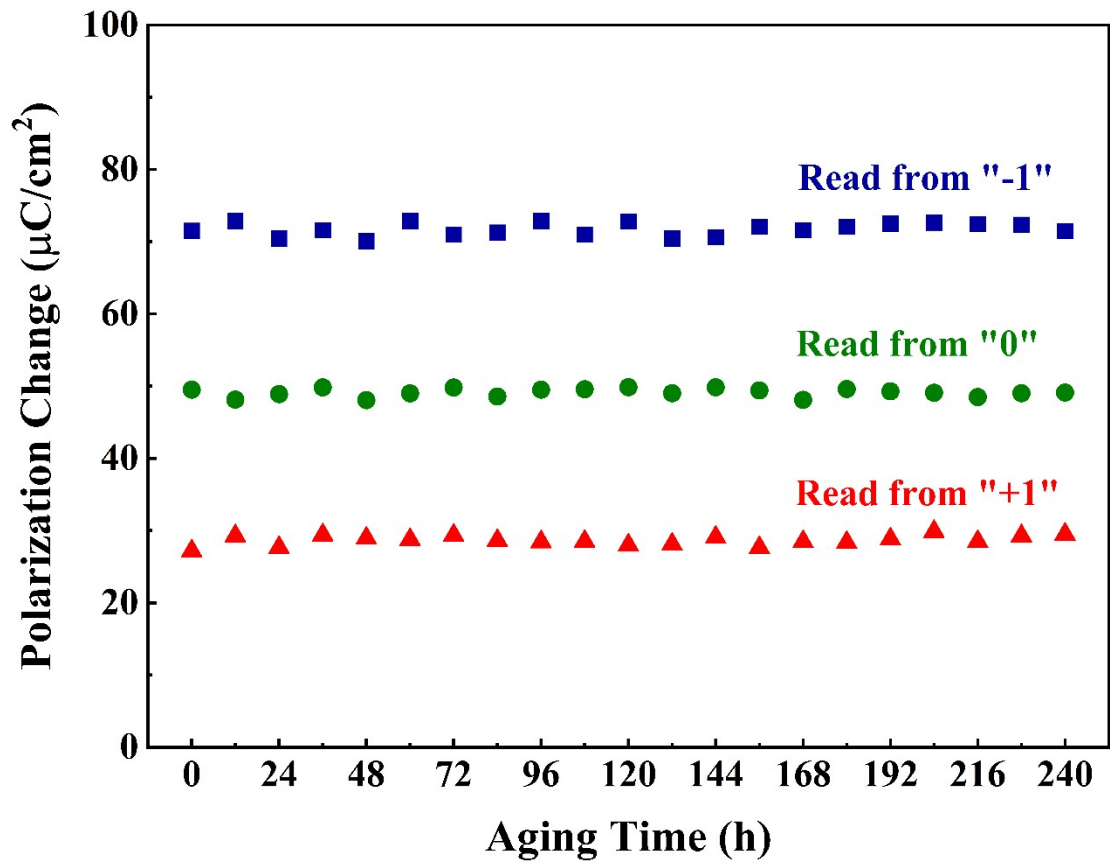


Fig. S7 The results of aging test: By repeating the write/read tests and recording the polarization change over the 10-day aging time.

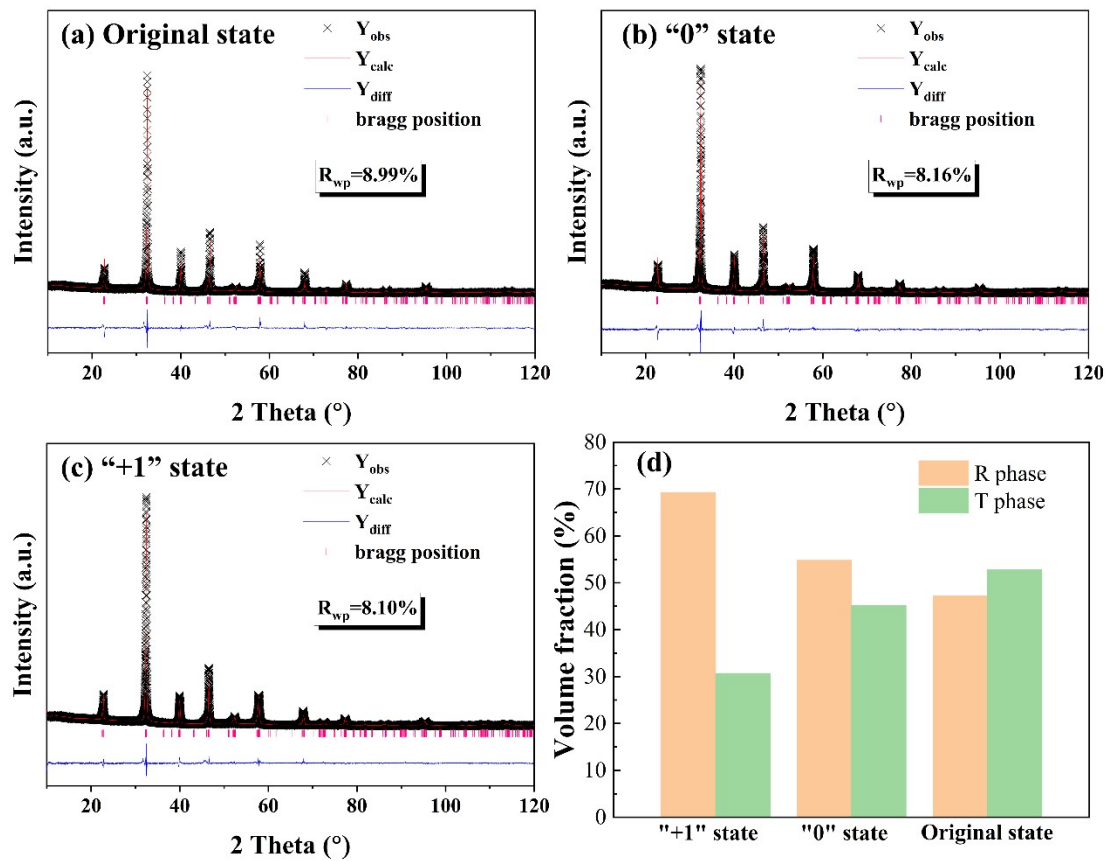


Fig. S8 XRD Rietveld refinement patterns of BNKT:3.0%Eu in different states: (a) Original state; (b) "0" state; (c) "+1" state; and (d) the corresponding calculated volume fractions of R phase and T phase when sample is in the above three states.